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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C23C 16/00, C08J 7/18, 14/00, B05D 3/00, H05H 1/24, B32B 9/04, 13/12	A1	(11) International Publication Number: WO 97/37053 (43) International Publication Date: 9 October 1997 (09.10.97)

(21) International Application Number: PCT/US97/05061

(22) International Filing Date: 28 March 1997 (28.03.97)

(30) Priority Data:
08/626,020 1 April 1996 (01.04.96) US

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(81) Designated States: AU, BR, CA, CN, JP, KR, SG, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: BARRIER FILMS HAVING VAPOR COATED HIGH ENERGY SURFACES

(57) Abstract

A method of producing a multilayer polymeric film is accomplished through the vapor deposition of an inorganic oxide coating onto an amorphous nylon layer, which is adhered to a polymeric substrate. A multilayer polymeric film exhibiting barrier characteristics is also accomplished through the use of an amorphous nylon layer between a vapor deposited inorganic oxide coating and a polymeric substrate.

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BARRIER FILMS HAVING VAPOR COATED HIGH ENERGY SURFACES

The present invention relates to barrier films and, in particular, to barrier films having at least one exposed high energy surface for receipt of a barrier coating through vapor deposition of a barrier coating material.

Coatings produced by vapor deposition are known to provide certain barrier characteristics to the coated substrate. For example, an organic coating such as a amorphous carbon can inhibit the transmission of elements such as water, oxygen, and carbon dioxide. Accordingly, carbon coatings have been applied to substrates (e.g., polymeric films) to improve the barrier characteristics exhibited by the substrate. Thus, the vapor deposited coating is often referred to as a barrier coating.

Another example of coatings applied to substrates to improve their barrier characteristics are coatings of inorganic materials, such as inorganic oxides. Oxides of silicon and aluminum are widely utilized to improve the barrier characteristics of substrates, especially polymeric substrates. Oxides of silicon and aluminum also provide abrasion resistance due to their glass-like nature.

The above-described coatings can be deposited on substrates through various techniques of vapor deposition. Typically vapor deposition techniques can be classified as either physical vapor deposition (PVD) or as chemical vapor deposition (CVD). Examples of PVD processes include ion beam sputtering and thermal evaporation. Examples of CVD processes include glow discharge and Plasma Enhanced Chemical Vapor Deposition (PECVD).

Of these techniques, PECVD is becoming widely utilized, in part, because it enables the coating of temperature sensitive substrates, such as polymeric films. Particularly, this technique allows the deposition of a coating material at lower reaction chamber temperatures, as compared to the reaction chamber temperatures required in other deposition

processes, e.g., glow discharge and more so, ion beam sputtering. As a result of the lower reaction chamber temperatures, temperature-sensitive substrates can be coated, which might otherwise be detrimentally affected by the higher reaction chamber temperatures found in the other coating processes.

The PECVD process is, however, a relatively slow and lengthy process, which in many cases renders such technique commercially impracticable. Accordingly, there exists a need in the art for a method that increases the rate of production of a barrier film utilizing PECVD, while at the same time maintaining the desirable barrier properties exhibited by the coated substrate.

There is also a continuing need in the art to provide barrier films with increased barrier characteristics. Accordingly, it is an object of the present invention to provide barrier films with improved barrier characteristics and a method of making the same.

The present invention, which addresses the needs of the prior art, provides a method for producing a polymeric film having barrier characteristics. The method includes the step of vapor depositing an inorganic oxide coating on an exposed surface of an amorphous nylon layer which is adhered to a polymeric substrate.

The polymeric substrate can be any polymeric substrate as long as its compatible with the amorphous nylon layer. Preferred polymeric substrates include polypropylene, polyethylene, biaxial nylon and polyester. The inorganic oxide coating can be any inorganic oxide coating capable of being vapor deposited onto a polymeric substrate. Preferred inorganic oxide coatings include oxides of silicon and aluminum, and more specifically, SiO_x, in which x is $1 \leq x \leq 2$, Al_2O_3 and mixtures thereof. The SiO_x coating is preferably formed by the decomposition of a silicon-containing compound. Optimally, the silicon-containing compound is decomposed in the presence of a plasma including a noble or inert gas. Preferred silicon-containing compounds include silanes, siloxanes and silanols.

The present invention also provides a method for increasing the production rate of a barrier film. The method includes the step of adhering an amorphous nylon layer to a polymeric substrate and thereafter vapor depositing an inorganic oxide coating on the exposed surface of the amorphous nylon layer. A preferred technique of adhering the amorphous nylon layer to the polymeric substrate is through coextrusion.

The present invention also provides a multilayer polymeric film having barrier characteristics. The film has a polymeric substrate with an amorphous nylon layer on one side of the polymeric substrate. An inorganic oxide coating is situated on the outside surface of the amorphous nylon layer, i.e., the side opposite from the polymeric substrate. The inorganic oxide coating preferably has a thickness from 10 to 5000 angstroms, and more preferably from 100 to 2000 angstroms.

As a result of the present invention, the time required to produce a polymeric film having a vapor deposited coating is greatly reduced, and thereby increases the commercial practicality of PECVD techniques. Moreover, the present invention provides a method of making a polymeric film having an improved barrier to the transmission of water and atmospheric gases when the coating time remains the same. Accordingly, the barrier films of the present invention provide improved impermeability to the elements such as water and atmospheric gases.

In accordance with the present invention, a method is provided for producing a polymeric film having barrier characteristics. The method includes the step of vapor depositing a barrier coating on an exposed surface of a polymeric material that provides a high energy surface, which is adhered to a polymeric substrate.

An example of a polymeric material that provides what is referred to as a "high energy surface" is amorphous nylon. It is believed that the surface of an amorphous nylon layer facilitates the adhesion of the vapor deposited coating

thereto, which in turn results in a better quality coating. Particularly, the exposed surface of the amorphous nylon layer exhibits a high "wettability" or surface energy in comparison to other polymers. The wettability of a polymer is believed to affect the ability of material to intimately contact another material. Thus, it is believed that the high wettability of the amorphous nylon skin layer facilitates the vapor deposition of a better quality barrier coating than can be achieved by directly coating the underlying polymeric substrate.

In this regard, it has been demonstrated herein that the application of a polymeric layer having a high energy surface (such as amorphous nylon) to a polymeric substrate greatly reduces the time required to deposit a barrier coating via vapor deposition, and more specifically, PECVD. The high energy surface enables a reduction in the coating time while maintaining barrier characteristics comparable to the prior art films.

The use of a high energy surface (such as amorphous nylon) also facilitates the production of a barrier film having increased or improved barrier characteristics if the coating time period remains the same. In other words, one of ordinary skill in the art can keep the coating time period at a constant and obtain a multilayer polymeric film with increased barrier characteristics. The effect of utilizing a high energy surface has also been observed to become more pronounced during short coating times, e.g., at coating rate of eight feet per minute (FPM) versus four FPM. This is believed to be due to the overall barrier characteristics exhibited by the film depending more on the quality of the coating than the quantity of the coating material applied.

The amorphous nylon employed in the present invention is preferably an amorphous co-polyamide synthesized from hexamethylenediamine and a mixture of isophthalic and terephthalic acids. One such commercially available product is Dupont PA-3426. By reference to an amorphous nylon, a nylon polymer that is substantially 100% amorphous is contemplated.

This can easily be ascertained by Differential Scanning Calorimetry (DSC) because the polymer should not exhibit any peaks that correspond to a crystalline region. However, it is also contemplated that blends of amorphous nylon with semi-crystalline nylons can be utilized as long as the blend exhibits a wettability comparable to that of the amorphous nylon.

The amorphous nylon layer can be adhered to the substrate by a variety of techniques known in the art. For example, the nylon layer can be laminated onto a polymeric substrate by use of an adhesive. One particularly preferred method of securing a nylon layer to a polymeric substrate is accomplished by co-extruding a polymeric material with amorphous nylon, thereby providing a polymeric substrate having a layer of amorphous nylon on at least one side. Typically, a tie layer is employed to adhere the amorphous nylon to the polymeric substrate. For example, a material such as maleic anhydride modified polypropylene can be employed as the tie layer. One such commercially available product is Atmer QF-500A.

It is also contemplated that other polymers exhibiting a similar wettability to that of amorphous nylon would also be effective in providing a high energy surface for receipt of a barrier coating by vapor deposition.

Examples of polymeric substrates to be utilized in accordance with the present invention include, but are not limited to, polypropylene, polyethylene, biaxial nylon and polyester. It is believed that other substrates can also be employed, as long as such substrates are compatible with the material exhibiting the high energy surface.

The present invention also provides a method for increasing the production rate of a barrier film. The method includes the steps of adhering a polymeric layer having at least one exposed high energy surface to a polymeric substrate and, thereafter vapor depositing a barrier coating on the exposed, high energy surface. Again, this polymeric layer is preferably an amorphous nylon layer.

As described earlier, the barrier coating is formed by

the vapor deposition of the barrier material. In accordance with the present invention, any material that can be vapor deposited and offer barrier properties can be utilized as the barrier coating. The barrier coating can be either an organic coating, such as a carbon coating, or an inorganic coating, such as an oxide coating. A preferred carbon coating is amorphous carbon, which is due in part to its barrier characteristics and ease of application. Preferred oxide coatings include oxides of silicon (SiO_x, in which $1 \leq x \leq 2$) and of aluminum (Al_2O_3). Moreover, mixtures of various coatings can also be utilized, e.g., SiO_x, in which $1 \leq x \leq 2$, and Al_2O_3.

Any vapor deposition technique can be utilized in accordance with the present invention, provided that the reaction chamber temperatures are not detrimental to the substrate being coated. Preferably, a CVD process is utilized because of the temperature sensitive nature of the polymeric materials. PECVD is most preferred because the reaction chamber temperatures are usually well below the melting points of the contemplated polymeric materials to be utilized as the substrate. This is due in part due to the low temperature plasma that is formed during the PECVD coating process.

PVD techniques usually require reaction chamber temperatures above the melting points of the contemplated polymeric substrates and, as a result, should normally be avoided. However, if the reaction chamber temperatures can be kept at a temperature that is not detrimental to the polymeric substrate, the PVD technique can of course be utilized in accordance with the present invention. As will be apparent to those skilled in the art, the source material for the barrier coating is dependent on the type of vapor deposition process utilized. In PVD processes the source material is usually the same chemical specie that is being deposited as the barrier coating. For example, a solid SiO_x source is placed within reaction chamber to be vaporized and is thereafter deposited as a SiO_x coating on the substrate.

In CVD processes, which are preferred, the source material is not the same chemical specie that is being

deposited as the coating. For example, gaseous reactants such as hexamethyldisiloxane (HMDSO) and oxygen (O_2) are placed in the reaction chamber to react and thereafter provide a SiO_x coating on the substrate. Thus, the main gaseous reactant, e.g., HMDSO, decomposes to form the desired coating on the substrate.

Because CVD coating processes are preferred, the source material for the barrier coating is preferably a gaseous reactant or a mixture of gaseous reactants. Alternatively, non-gaseous source materials can be utilized provided that they can be transformed to a gaseous state, e.g., vaporized or sublimed.

The deposition of an amorphous carbon coating requires a carbon source as the gaseous reactant. Preferably, the gaseous reactant is a hydrocarbon having from 1 to 20 carbon atoms. Acetylene is one such preferred gaseous reactant.

Similarly, the deposition of a SiO_x coating, in which $1 \le x \le 2$, requires a silicon-containing compound and an oxidizing agent as the gaseous reactants. Examples of these silicon-containing compounds include, but are not limited to, silanes, siloxanes and silanols. Hexamethyl-disiloxane and tetraethoxylsilane (TEOS) are two such preferred gaseous reactants. Oxidizing agents include, but are not limited, molecular oxygen (O_2) and nitrous oxide (N_2O). However, other sources for atomic oxygen can be readily utilized.

The deposition of an aluminum oxide coating requires an aluminum-containing compound and an oxidizing agent. An example of an aluminum-containing compound is aluminum chloride ($AlCl_3$). The oxidizing agents can be the same as previously described for the deposition of an SiO_x coating.

Overall, once a particular barrier coating has been selected, one of ordinary skill in the art can easily be ascertain the gaseous reactants required to vapor deposit the barrier coating.

Upon the introduction of the gaseous reactant to the reaction chamber, the main gaseous reactant decomposes or reacts with other gaseous reactants and is thereafter

deposited on the exposed high energy surface as a barrier coating. This coating may range in thickness from 10 to 5000 angstroms, preferably from 100 to 2000 angstroms. The thickness of the coating will be primarily dependent on the amount of time allowed for deposition.

The plasma utilized with the present invention is preferably generated by the application of a primary radio frequency to a first electrode. This radio frequency excites the gas mixture flowing through the chamber, thereby forming a plasma. This gas mixture is preferably a mixture of the gaseous reactants mentioned above, e.g., acetylene or TEOS and oxygen, and an inert or noble gas such as argon or helium.

Apparatuses adapted for vapor deposition, and more specifically PECVD, are well known and commercially available. Such apparatuses generally include a chamber sized for receipt of a substrate. The apparatus additionally includes a vacuum pump for evacuating the chamber, means for introducing a gas mixture to the chamber under controlled conditions, and means for generating a plasma within the chamber.

In one particularly preferred embodiment, the plasma generation means includes distally spaced first and second electrodes, which together can be employed to introduce independent dual energy sources into the reaction chamber. A primary radio frequency of 13.56 MHZ is applied to the first electrode and a secondary radio frequency of 90 KHz to 450 KHz is applied to the second electrode. Preferably, the chamber serves as the ground for both radio frequencies.

The primary frequency generates the plasma (by exciting the gas mixture), while the secondary frequency is believed to facilitate the deposition of the carbon on the high energy surface by exciting the molecules of the coating material being deposited. This rationale is supported by the fact that a visible change in the plasma is observed upon application of this second radio frequency.

Other means of generating the plasma are also contemplated. For example, a primary frequency in the microwave range, e.g., 2.45 GHz, can also be utilized. In addition,

photometric means such as lasers can be employed to excite the gas mixture. Magnets can also be utilized to aid in directing the coating material to the substrate.

The chamber also includes a substrate holder plate for supporting the polymeric substrate to be coated. This substrate holder plate is preferably integral with the second electrode. In addition, the substrate holder plate may include either a flat or an arcuate support surface. It is contemplated that the use of an arcuate support surface would facilitate commercial production of the present invention.

EXAMPLE 1

Two amorphous carbon coated control films were produced. A 1 mil thick oriented polypropylene film approximately 27.94 cm (11") long by 39.37 cm (15.5") wide was placed on a 25.4 cm (10") long by 39.37 cm (15.5") wide substrate holder plate attached to the second electrode. The substrate holder plate included an arcuate surface having a 101.6 cm (40") radius of curvature. The film overhung the substrate holder plate along the length of such film to allow the film to be secured to the holder.

The chamber was pumped down to 1 mTorr. An acetylene/argon gas mixture was then introduced into the chamber at a flow rate of 100 sccm, 70% of the mixture being acetylene. The pressure within the chamber was increased to a reaction pressure of 100 mTorr by use of a gate valve located at the inlet of the vacuum pump. A primary frequency of 13.5 MHZ at a power level of 100 watts was applied to the first electrode and a secondary frequency of 95 kHz at a power level of 25 watts was applied to the second electrode.

The substrate was coated for approximately 300 seconds. Thereafter, the gas mixture was shut off and the chamber was pumped down again to 1 mTorr. The chamber vacuum was then broken by bleeding in dry nitrogen gas and the respective coated substrate was removed.

The two control films were thereafter tested. The first control film exhibited an oxygen transmission rate (TO_2) of 0.4 cc O_2/645.16 cm^2($100in^2$)/atm/24hr at 23°C and 0% relative

humidity and a water vapor transmission rate (WVTR) of 0.02 g H_2O/645.16 cm^2(100in^2)/atm/24hr at 37.8°C (100°F) and 90% relative humidity. The second control film exhibited an oxygen transmission rate of 0.6 cc O_2/645.16 cm^2(100in^2)/atm/24hr at 23°C and 0% relative humidity and a water vapor transmission rate of 0.09 g H_2O/645.16 cm^2(100in^2)/atm/24hr at 37.8°C (100°F) and 90% relative humidity.

Accordingly, the average control oxygen transmission rate was 0.5 cc O_2/645.16 cm^2(100in^2)/atm/24hr at 23°C and 0% relative humidity and the average control water vapor transmission rate was 0.055 g H_2O/645.16 cm^2(100in^2)/atm/24hr at 37.8°C (100°F) and 90% relative humidity.

EXAMPLE 2

Amorphous carbon coated barrier films in accordance with the present invention were produced utilizing a base sheet formed by co-extruding amorphous nylon with polypropylene that was subsequently biaxially oriented. Resin pellets of Dupont nylon PA-3426 were employed, along with a tie layer of Atmer QF-500A. The oriented film was approximately 1 mil thick, the amorphous nylon layer representing approximately 6% or .06 mils of the total film thickness.

A polymeric sample approximately 27.94 cm (11") long by 39.37 cm (15.5") wide was placed on the substrate holder plate attached to the second electrode and described above in Example 1.

The chamber was pumped down to 1 mTorr. An acetylene/argon gas mixture was then introduced into the chamber at a flow rate of 60 sccm, approximately 83% of the mixture being acetylene. The pressure within the chamber was increased to a reaction pressure of 100 mTorr by use of a gate valve located at the inlet of the vacuum pump. A primary frequency of 13.5 MHZ at a power level of 100 watts was applied to the first electrode and a secondary frequency of 95 kHz at a power level of 25 watts was applied to the second electrode.

The substrate was coated for approximately 60 seconds. Thereafter, the gas mixture was shut off and the chamber was pumped down again to 1 mTorr. The chamber vacuum was then

broken by bleeding in dry nitrogen gas and the respective coated substrate was removed.

The polymeric sample was thereafter tested. The sample film exhibited an oxygen transmission rate of 0.42 cc O_2/645.16 cm^2($100in^2$)/atm/24hr at 23°C and 0% relative humidity and a water vapor transmission rate of 0.024 g H_2O/645.16 cm^2 ($100in^2$)/atm/24hr at 100°F and 90% relative humidity.

Additional polymeric samples were prepared under varying test conditions. The measured results from all of the polymeric samples, i.e., samples 1-8, are set forth in Table 1:

Table 1

SAMPLES	TO_2	WVTR	PRESSURE (mTorr)	FLOW C2H2	FLOW Ar	PRIMARY POWER (watts)	SECONDARY POWER (watts)	TIME (sec.)
Control 1	0.4	0.02	100	70	30	100	25	300
Control 2	0.6	0.09	100	70	30	100	25	300
Sample 1	0.42	0.024	100	50	10	100	25	60
Sample 2	0.18	0.005	100	50	10	50	25	60
Sample 3	0.11	0.015	100	50	10	75	25	60
Sample 4	0.10	0.024	100	50	10	75	25	45
Sample 5	0.18	0.020	100	50	10	75	25	30
Sample 6	0.26	0.062	100	50	10	75	25	15
Sample 7	0.07	0.036	150	50	10	75	25	30
Sample 8	0.09	0.051	100	50	10	50	25	30

TO_2: cc/645.16 cm^2(100 in^2)/atm/24hr at 23°C and 0% R.H.
WVTR: g/645.16 cm^2(100in^2)/atm/24hr at 100°F and 90% R.H.
FLOW: Standard cubic centimeter (sccm)

It is readily apparent from the test data set forth above that a barrier film can be produced by the deposition of carbon on an exposed high energy surface of an amorphous nylon layer. It is particularly significant that the rate of producing such a barrier film can be increased by approximately a factor of 10, i.e., the coating time is decreased from approximately 300 seconds to 15 to 60 seconds. It is also significant that the resultant film exhibits a markedly decreased oxygen transmission rate, while improving, or at the minimum maintaining, the level of water transmission.

Example 3

A SiO_x control film was produced, in which $1 \leq x \leq 2$, utilizing the stock 1 mil OPP film material described in Example 1. After the coating process, samples from the film were thereafter tested for oxygen and water vapor transmission. The SiO_x coated film exhibited an oxygen transmission rate of 1.54 cc O_2/645.16 cm^2($100in^2$)/atm/24hr at 23°C and 0% relative humidity (hereinafter cc/645.16 cm^2($100in^2$)/atm/24hr), and a water vapor transmission rate of 0.06 g H_2O/645.16 cm^2($100in^2$)/atm/24hr at 37.8°C (100°F) and 90% relative humidity (hereinafter g/645.16 cm^2($100in^2$)/atm/24hr).

Example 4

A SiO_x coated film in accordance with the present invention was produced, in which $1 \leq x \leq 2$, utilizing the stock amorphous nylon-OPP film material described in Example 2. The reaction parameters and coating time were identical to those utilized in Example 3. After the coating process, samples from the film were thereafter tested for oxygen and water vapor transmission. The SiO_x coated film exhibited an oxygen transmission rate of 0.13 cc/645.16 cm^2($100in^2$)/atm/24hr, and a water vapor transmission rate of 0.07 g/645.16 cm^2 ($100in^2$)/atm/24hr.

From the results in Examples 3 and 4, it is readily apparent that the use of a high energy surface, such as that provided by the amorphous nylon layer, is applicable to other vapor deposited coatings, such as inorganic oxides. In particular, the oxygen permeability of the barrier film

decreased by a factor of 10 through the use of the amorphous nylon skin. The SiO_x coated OPP film in Example 3 exhibited an oxygen transmission rate of 1.54 cc/645.16 cm^2 ($100in^2$)/atm/24hr. While on the other hand, the SiO_x coated amorphous nylon-OPP film in Example 4 exhibited an oxygen transmission rate of 0.13 cc/645.16 cm^2 ($100in^2$)/atm/24hr. Accordingly, Examples 3 and 4 illustrate that when reaction parameters are kept at a constant, barrier films with increased barrier characteristics are obtained.

The results from Examples 3 and 4 also illustrate the synergistic effect produced by the high energy surface of the amorphous nylon layer. This effect is seen by comparing the magnitudes of reduction in the oxygen transmission rates for the OPP film versus the amorphous nylon-OPP film. The stock OPP film has an oxygen transmission rate of 100 cc/645.16 cm^2 ($100in^2$)/atm/24hr, which was reduced to 1.54 cc/645.16 cm^2 ($100in^2$)/atm/24hr after the application of a SiO_x coating. The stock amorphous nylon-OPP film has an oxygen transmission rate of 50.5 cc/645.16 cm^2($100in^2$)/ atm/24hr, which was reduced to 0.13 cc/645.16 cm^2($100in^2$)/atm/24hr after the application of a SiO_x coating. Stated otherwise, the OPP film exhibited approximately a 65-fold reduction in its oxygen transmission rate. The amorphous nylon-OPP film exhibited approximately a 388-fold reduction in its oxygen transmission rate. Thus, the high energy surface of the amorphous nylon layer facilitated the deposition of a barrier coating approximately 600% less permeable than could be achieved by directly coating the underlying polymeric material.

CLAIMS:

1. A method for producing a polymeric film having barrier characteristics, which comprises:

vapor depositing an inorganic oxide coating selected from the group consisting of SiO_x, wherein x is $1 \leq x \leq 2$, Al_2O_3 and mixtures thereof on an exposed surface of an amorphous nylon layer, wherein said amorphous nylon layer is adhered to a polymeric substrate formed of a material selected from the group consisting of polypropylene, biaxial nylon, polyester and polyethylene.

2. The method according to Claim 1, wherein said inorganic oxide coating is SiO_x vapor deposited by the decomposition of a silicon-containing compound in the presence of a plasma including an inert or noble gas.

3. The method of Claim 2, wherein said silicon-containing compound is selected from the group consisting of silanes, siloxanes and silanols.

4. A method for increasing the production rate of a polymeric film having barrier characteristics, which comprises:

adhering an amorphous nylon layer having at least one exposed surface to a polymeric substrate formed of a material selected from the group consisting of polypropylene, biaxial nylon, polyester and polyethylene; and thereafter,

vapor depositing an inorganic oxide coating selected from the group consisting of SiO_x, wherein x is $1 \leq x \leq 2$, Al_2O_3 and mixtures thereof on said exposed surface of said amorphous nylon layer.

5. The method according to Claim 4, wherein said inorganic oxide coating is SiO_x vapor deposited by the decomposition of a silicon-containing compound in the presence of a plasma including a noble or inert gas.

6. The method of Claim 5, wherein said silicon-containing compound is selected from the group consisting of silanes, siloxanes and silanols.

7. A multilayer polymeric film having barrier characteristics comprising a polymeric substrate formed of a material selected from the group consisting of polypropylene, biaxial nylon, polyester and polyethylene; an amorphous nylon layer on one side of said substrate; and a vapor deposited inorganic oxide coating selected from the group consisting of SiO_x, wherein x is $1 \leq x \leq 2$, Al_2O_3 and mixtures thereof on the side of said amorphous nylon layer opposite that is said polymeric substrate.

8. The multilayer polymeric film according to Claim 7, wherein said inorganic oxide coating is an inorganic oxide coating of 10 to 5000 angstroms.

9. The multilayer polymeric film according to Claim 8, wherein said inorganic oxide coating is an inorganic oxide coating of 100 to 2000 angstroms.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/05061

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :Please See Extra Sheet.
US CL :Please See Extra Sheet.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: vapor deposition, plasma, inorganic or organic coatings, oxides, amorphous carbon, ethylene vinyl alcohol, nylon

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,E	US 5,626,947 A (HAUER et al) 06 May 1997, col. 4, lines 33-66, col. 6, lines 34-40.	1-9
Y	US 5,496,595 A (UEDA et al) 05 March 1996, col. 3, line 1, col. 5, lines 4 and 41, col. 6, lines 6-12.	1-9
A	US 4,756,964 A (KINCAID et al) 12 July 1988.	1-9
A	US 5,084,356 A (DEAK et al) 28 January 1992.	1-9
A	US 5,085,904 A (DEAK et al) 04 February 1992.	1-9
A	US 5,137,780 (NICHOLS et al) 11 August 1992.	1-9

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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14 JULY 1997	04.08.97

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Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/05061

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C23C 16/00; CO8J 7/18, 14/00; B05D 3/00; H05H 1/24; B32B 9/04, 13/12

A. CLASSIFICATION OF SUBJECT MATTER:
US CL :

427/248.1, 249, 255.1, 255.2, 255.3, 255.6, 489, 491, 523, 525, 527, 529, 530, 563, 564, 566, 567, 568, 576, 577, 579; 428/446, 447, 451, 474.9, 475.2, 476.1,

B. FIELDS SEARCHED
Minimum documentation searched
Classification System: U.S.

427/248.1, 249, 255.1, 255.2, 255.3, 255.6, 489, 491, 523, 525, 527, 529, 530, 563, 564, 566, 567, 568, 576, 577, 579; 428/446, 447, 451, 474.9, 475.2, 476.1,